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S. B. SWEETSER ET AL

2,652,319

PROCESS FOR WATER-GAS GENERATION

Filed Jan. 3, 1949

2 Sheets-Sheet 1

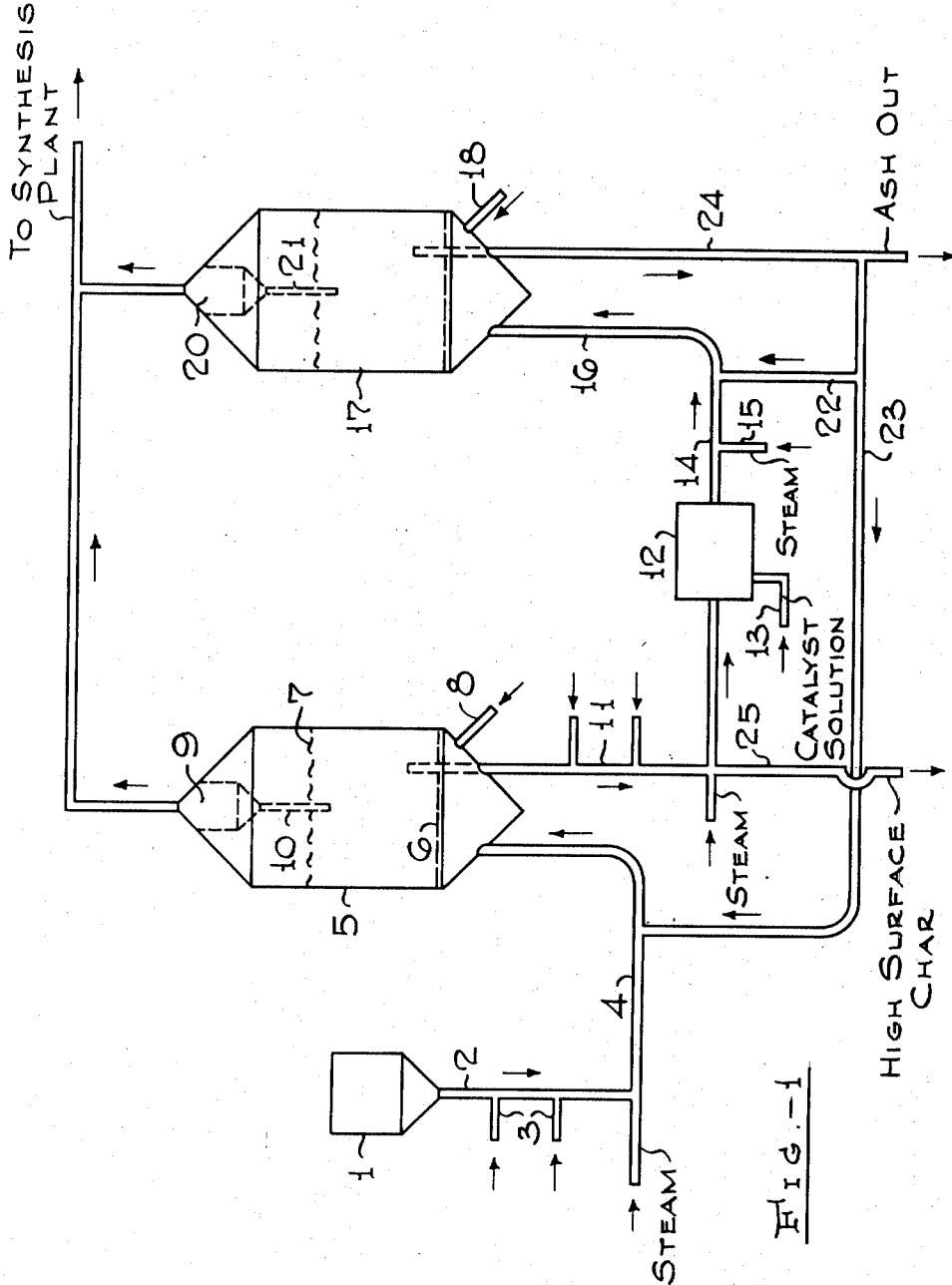


FIG. 1

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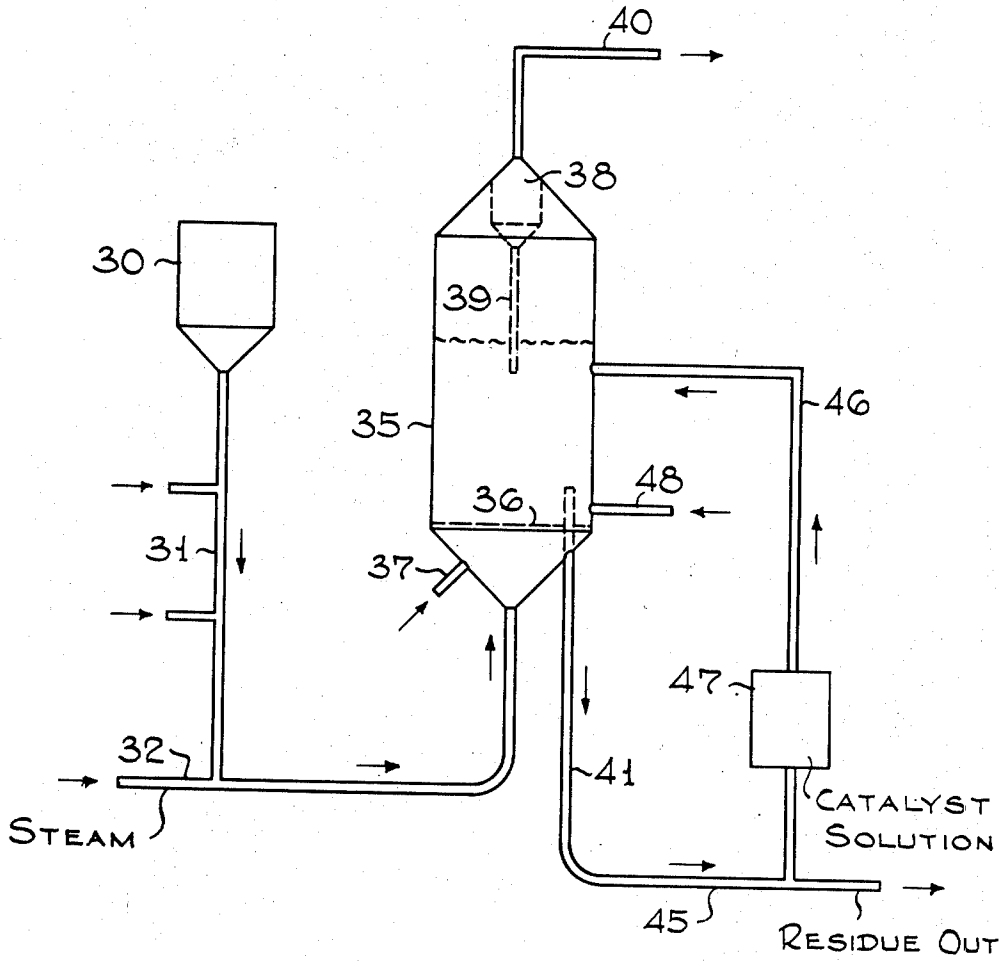


FIG.-2

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PROCESS FOR WATER-GAS GENERATION

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8 Claims. (Cl. 48-206)

1

The present invention relates to the enhancement of catalytic activity of catalyst agents when supported on a char carrier. The invention relates more particularly to the production of gases from non-gaseous carbonaceous material, and specifically to the production of gas mixtures containing carbon monoxide and hydrogen, such as water gas, from such carbonaceous materials as coke and coals.

It has long been known that solid fuel materials, such as coke, coal, and the like, may be converted into more valuable gases which can more easily be handled and more efficiently utilized for a greater variety of purposes. One of the most widely practiced gas-generating conversions is the so-called water-gas process in which solid fuels, such as coal or coke of any origin, are reacted with steam at temperatures of about 1400° to 2000° F. to produce water gas mixtures of carbon monoxide and hydrogen in varying proportions, depending mainly on the time of contact, conversion temperatures, and steam feed rate. The over-all water gas reaction being endothermic, heat must be supplied; this is usually accomplished by the combustion of a portion of the carbonaceous feed with an oxidizing gas, such as oxygen, at about 1600°-2400° F. The combustion reaction may be carried out either simultaneously with the water gas reaction or alternately in a make-and-blow fashion.

The water gas process permits the production of gas mixtures of varying composition and B. t. u. content. The process as such, therefore, is suited not only for the production of fuel gases but also for the production of gases for hydrogenation processes and particularly for the catalytic synthesis of hydrocarbons and oxygenated organic compounds from CO and H₂, which process requires H₂:CO ratios, depending on the products desired and reaction conditions to be maintained, varying within limits of about 0.5 to 2.5 or more volumes of H₂ per volume of CO.

The technical utilization of the water gas process, particularly for hydrogenation and for production of synthesis gas has been impeded by difficulties encountered particularly in heat supply, continuity of operation, and limitations in temperature imposed by low ash fusion or softening points. The problem of continuity of operation has been satisfactorily solved heretofore by the application of the fluid solids technique wherein the carbonaceous charge is reacted in the form of a dense turbulent mass of finely divided solids fluidized by the gaseous reactants and products. Heat is generated either by partial

2

combustion of carbonaceous materials within the gas generator or a continuous circulation of suspended solid carbonaceous material to a separate heater in which heat is generated by combustion of the carbonaceous constituents of the residue, and recirculation of the highly heated fluidizable combustion residue to the gas generation zone to supply the heat required therein.

Whether heat is generated within the gas generator by combustion or whether it is supplied as sensible heat of the recirculated solids, it is generally desirable to operate the water-gas generating unit at as low a temperature as possible commensurate with obtaining high yields of H₂ and CO. Thus at the higher temperature ranges, ash tends to become plastic, making fluidization difficult. Also, at the higher temperature ranges, the heat resistance of economical construction materials available for fluid solids equipment decreases substantially. Thus though the highest yields may be obtained at 2000° F. and above, prolonged operation at these high temperatures is increasingly accompanied by fluidization difficulties and weakening of structural materials.

However, as the operational temperatures are decreased, not only are the yields of CO and H₂, and the rate of formation of these gases, also decreased, but also, in accordance with equilibrium considerations, the rate and quantity of CO₂ formed is increased. These factors have been recognized and efforts have been directed towards finding catalysts which permit lower temperatures of operation to obtain high yields of H₂ and CO from the water gas reaction, and produce these gases at high rates. Thus it has been determined in laboratory experiments that the carbonates of sodium and potassium caused the water gas reaction to take place some 180° F. lower and the carbon monoxide content of the gases was found to be higher than without the use of catalyst. When, however, this technique was transferred to larger scale operations, it was found that impregnating fresh coke or coal with catalyst and then subjecting the impregnated mass to the water gas reaction using the fluid solids technique gave but indifferent results, and showed neither marked reduction of temperature requirements for producing water gas nor increased reaction rates at lower temperatures.

These observations have also been confirmed in experimental operations involving the use of the fluidized solids technique. When a catalytic material such as sodium or potassium carbonate is impregnated on fresh coal or coke, there is little tendency for the catalyst to be adsorbed on the

coal or coke and it is sufficiently volatile at the temperature of operation so that it is readily lost from the reaction zone by the stripping action of the product gases.

The present invention overcomes the aforementioned difficulties and affords various additional advantages. These advantages, the nature of the invention, and the manner in which it is carried out, will be fully understood from the following description thereof read with reference to the accompanying drawing.

It is, therefore, the principal object of the present invention to provide an improved process for the production of gas mixtures containing carbon monoxide and hydrogen.

Another object of the invention is to provide a process for the commercial production of water gas from carbonaceous materials and steam involving the efficient and effective utilization of a catalyst promoting the gasification of carbon.

A more specific object of the invention is to provide an improved process for pretreating carbonaceous material such as coke or coal prior to impregnation to provide a highly active surface for catalyst impregnation.

Other objects and advantages of the invention will appear hereinafter.

It has now been found that these objects may be accomplished by employing in a fluid solids gas generator solid carbonaceous charging material of high surface area and chemical reactivity in conjunction with a catalyst promoting the gasification of carbon. In this manner, the steam conversion at a given temperature and under otherwise equal conditions may be considerably increased and the gas generator may be operated at temperatures considerably below the gas generation temperatures required for other feed materials under similar conditions of pressure, steam concentration, contact time, carbon concentration, etc., without detrimentally affecting the steam conversion.

Experimental research employing the fluidized solids technique has now established that whereas fresh coke or coal has a very small surface area, after use for a relatively short period of time in the fluid water gas generator to produce water gas, the carbonaceous material develops a very large surface area of the order of 500-800 square meters per gram. This has been most noticeable in the case of low temperature coke, such as "Disco" coke, and coke produced by the fluid solids carbonization of coal at 800°-1000° F. Thus it has been found that the surface area of a low-temperature coke undergoing gasification in the fluid water gas generator goes through a maximum, as shown by the following tabulation:

Surface area vs. coke carbon content

Percent Carbon	Surface Area, M ² /gm.
84% (Fresh)	0.04
56	680
27	360
17	200
5	60

From this table it is readily seen that coke or coal, though initially having very low surface area, develops a high surface area after a relatively minor portion of its carbon content has been removed by gasification, corresponding to a relatively short period of time.

This discovery has now been applied to the

fluid catalytic gasification of coke or coal by means of the water gas reaction. Instead of impregnating fresh coke or coal with the gasification catalyst, as practiced by the prior art, in accordance with the present invention a highly active coke or coal is first produced, having a high surface area, and this material of high surface area, over 10,000-20,000 times as high as the fresh coke or coal, is then impregnated with the gasification catalyst. Because of the high surface area and the strong adsorption forces associated therewith, the impregnated catalyst is firmly held on the surface of the carbonaceous material despite the high temperature and the stripping action of the gases in the generator. Also, the uniformity of impregnation and the amount of catalyst that is associated with each unit of carbon is of a substantially higher order of magnitude than is the case with fresh coke or coal impregnated with catalyst, and as a result the catalytic effect of the gasification promoter is greatly enhanced as compared with the impregnation of the promoter on the untreated coal or coke feed.

In one form of operation of the process according to the present invention, employing the fluidized solids technique, the operation is carried out in three steps involving two stages of gasification and an impregnation step. In the first stage steam and oxygen are injected into a reactor containing a fluidized bed of coal or coke under suitable conditions of temperature and pressure to obtain a conventional water gas reaction, with the oxygen being the combustion agent for supplying the heat of reaction. Fresh coke or coal is added to the first stage generator as required to maintain the desired inventory of the system. At the desired level of high surface area of the solids within the generator, corresponding to a relatively short contact time, coke is continuously withdrawn from the water gas generator and is impregnated with a suitable catalyst, for example, sodium carbonate, to the extent of about 0.1 to 3% by weight of the coke. The impregnated coke is then sent to a second gasification stage wherein the carbon content is reduced to any desired level to produce high yields of CO and H₂ at moderate gasification temperatures.

Water gas may be generated by the so-called one or two vessel systems, depending upon how the heat requirements for the system are provided. "One vessel" refers to a water gas generation unit in which heat is produced within the gasification zone by an exothermic oxidation reaction. In a "two vessel" system, heat is generated in a separate exothermic reaction zone and transferred by the circulation of solids to the gasification zone of the water gas generation unit. In the present invention, any one-vessel or two-vessel water gas generation units may be operated individually or in stages.

Having set forth its general nature and objects, the invention will best be understood from the subsequent more detailed description in which reference will be made to the accompanying drawings which illustrate a system suitable for carrying out a preferred embodiment of the invention.

Figure I is a diagrammatic representation of a two-stage water gas generation system. For illustrative, but not limiting purposes, both stages incorporate so-called "one-vessel" systems for water gas generation. It is understood that the two stages may comprise two "one-vessel" systems, two "two-vessel" systems or any combination of such systems.

5

Figure II represents another embodiment of the invention wherein a single stage water gas generator comprising a one or two vessel system may be employed to carry out a modification of the invention.

Referring now to Figure I, fresh coke or coal ground to a finely divided form, preferably capable of passing through a 60 mesh screen and even through a hundred mesh screen, is fed from a supply hopper 1 into a standpipe 2 which is provided with a plurality of taps 3 through which slow currents of an aerating gas such as air, flue gas, synthesis tail gas, etc. may be injected in order to aerate the coke or coal. The suspension after preheating by means not shown is introduced into line 4 wherein it is dispersed and suspended in a stream of superheated steam. The mixture of fresh coke or coal and steam is discharged into the bottom of water gas generator 5, the suspension entering below grid 6 and then passing upwardly. In some designs it may be unnecessary to employ a grid. Due to the superficial velocity of said steam, which is maintained within the limits of from about 0.2 to 3 feet per second, the coke or coal is formed into a dense, turbulent ebullient mass, having a well-defined upper level 7. An oxidizing gas such as oxygen, is admitted through line 8, and may also be added to the stream in line 4. The steam and carbonaceous material react to form water gas, a gasiform product containing CO and H₂. The temperature in this non-catalytic zone is in the order of 1500° to 2000° F. and the gas pressure is preferably from 15 to 100 p. s. i. g., though pressure up to 400 p. s. i. g. and above may under certain conditions be employed. The heat required for the reaction is furnished substantially by the combustion of part of the carbonaceous solids in reactor 5 by the oxygen admitted through lines 8 and/or 4. The total supply of oxygen is carefully controlled to generate sufficient heat by combustion to satisfy the heat requirements of the process.

The gaseous products are withdrawn from generator 5 through a dust separator 9, such as a cyclone which has a dip pipe 10 extending below upper level 7 of the fluidized bed for returning entrained dust particles. The water gas may be treated for the removal of sulfur or other impurities and then delivered to storage, preferably after combination with the product from the catalytic second stage water gas generator 17.

The hot carbonaceous solids, now coke, are allowed to remain within reactor 5 for a sufficient period of time to attain the surface area desired, usually greater than 500 square gram meters, and then the hot carbonaceous solids are continuously withdrawn from water gas generator 5 through aerated bottom draw-off line 11 which extends above grid 6. The period of residence of the coke within reactor 5 to form the high surface area desired, depends upon a plurality of operating factors, such as type of coal fed, temperature of gas generation, ratio of steam to carbon, solids hold-up time, etc. The withdrawn solids are passed with the aid of steam to impregnation unit 12, which comprises a means suitable for impregnating finely divided carbonaceous solids with chemicals. One preferred method for accomplishing this consists of spraying a solution of the catalyst onto the char passing through the transfer line connecting both stages. Other methods may be employed in any known manner such

6

as by mixing, evaporating, decanting, etc. In unit 12 the high surface area coke is impregnated preferably with an aqueous solution of sodium carbonate. Other suitable catalytic materials may be potassium carbonate and zinc chloride, and as a result of the impregnation the coke contains 0.1 to 3% by weight of salt. Carbonate solution of the desired concentration may be admitted to 12 through line 13.

The impregnated char passes from impregnation unit 12 through line 14. Steam for suspending may be admitted through line 15. The suspended stream is passed through line 16 into the lower portion of a water gas generator 17 which is of essentially the same type as vessel 5 and is fitted at its lower end with an inlet line 18 for admitting oxidizing gas, preferably oxygen. Said oxidizing gas may also be added to the fluidized stream in line 15.

As in reactor 5, the fluidized impregnated carbonaceous material in generator 17 is in the form of a dense, turbulent mass fluidized by the upwardly flowing gases and superheated steam. Because of the catalytic effect, the gasification of the carbon by the steam in the catalytic reactor proceeds rapidly to form CO and H₂. The heat required for the endothermic gasification reaction in this "one-vessel" unit is supplied by the combustion of part of the carbonaceous solids in reactor 17 by the oxygen admitted through lines 18 and/or 15. The total supply of oxygen is carefully controlled to generate sufficient heat by combustion to satisfy the heat requirements of the process. The temperature maintained in catalytic reaction zone 17 is in the range of about 1300° to 1800° F., which is substantially lower than that required for high steam conversion without the use of a gasification catalyst. Because of the higher rates of conversion associated with the use of the catalyst, substantially smaller reactors may be employed to obtain over-all yields of the same order of magnitude as those obtained without catalyst with large reactor volumes.

The gasification products are withdrawn overhead through a dust separator 20 and line 21 and may go directly to product storage, to purification for sulfur removal and to a hydrocarbon synthesis plant after blending with the gasification products from the primary water gas reactor, or may be used as a fuel gas.

With catalytic reactor 17 the bulk of the gasification is accomplished, and the coke is consumed in the gasification reaction to any desired residual carbon content.

Ash of relatively low carbon content and surface area is continuously withdrawn from reactor 17 through line 24. If desired, the carbon associated with the ash may be completely utilized by combustion in a separate burner vessel (not shown) wherein the ash is burned at a temperature at least 100° F. above the temperature level in the gasification zones, and the hot residue recycled to the latter zones to furnish sensible heat. Also, since the catalyst content of the ash is very high, it may be desirable to recycle a minor portion, say 5-25%, thereof, to generators 5 and 17 via lines 22 and 23 to furnish a portion of the catalyst requirements of the system.

In Figure II there is shown another embodiment of the invention wherein a high surface area is provided for catalyst activation without operating in two stages.

Referring now to this figure, fresh coke or coal

ground to the desired fluidizable size is withdrawn from hopper 30 to aerated standpipe 31. The aerated material after preheating by means not shown is introduced into line 32 wherein it is further dispersed and suspended in a stream of superheated steam and oxygen. The mixture of steam, and fresh coke or coal is discharged into the lower conical portion of cylindrical gas generator 35, and passes upwardly through distributing grid member 36.

The gas generator is maintained at a temperature of between about 1300° and 1800° F., preferably about 1400° to 1700° F. and at a pressure of about 15 to 400 p.s.i.g. to permit the water gas reaction to take place between the steam and the coke maintained in a dense, ebullient bed. The heat required for the water gas reaction is supplied by combustion of a portion of the carbonaceous solids by oxygen introduced through line 37 or in part through line 32, though again, if desired, the heat may be supplied in part or whole by recirculating hot residue from a combustion zone (not shown).

Material is withdrawn from reactor 35 through line 41. Part of said material is rejected from the system through line 45. The unrejected portion is recycled to the reactor through impregnation unit 47 in which a solution of catalyst is sprayed onto the moving solid stream in a manner similar to that shown in the impregnation unit shown for the two stage process. The impregnated material is then passed through line 46 back to reactor 35. The material rejected from the system through line 45 may be leached for recovery of catalytic constituents, or in some cases when it has high residual carbon of high surface area it may be used for adsorbent or catalytic purposes, or in cases when it has low residual carbon content it may be burned or discarded as ash.

An alternative method of impregnating the catalyst on the char is to inject a stream of a solution of the catalyst directly into reactor 35 through line 48.

A gas consisting mainly of CO and H₂ is taken overhead from generator 35 and freed in gas-solids separator 38 from entrained fines which may be returned through pipe 39 to the dense phase. The gas is passed through line 40 and may be employed, after heat exchange and cooling, for the catalytic production of liquid hydrocarbons or as a fuel gas.

It will be understood that the embodiments of the invention as described above admit of numerous modifications apparent to those skilled in the art. Thus any catalyst promoting the gasification of carbon, such as K₂CO₃, ZnCl₂, carbonates of alkali and alkaline earth metals, etc., may be employed as well as Na₂CO₃. Heat exchange systems may be installed in the process to effect heat economies and adjust temperatures in the respective zones. The manner of conveying solids in an aerated or fluidized condition has been omitted in various instances for the sake of simplicity. Furthermore, though the present invention has been illustrated in its application to catalyzing the water gas reaction, it is also within the scope of the invention generally to disclose a process for enhancing catalytic effects by impregnating the char with promoters after a high surface area has been produced from coke or coal. Material suitable for this purpose is that removed by line 25 in Figure I and line 45 in Figure II. Thus for example, a highly active sulfactive hydrogen-

ation catalyst may be prepared by first subjecting coke or coal to a water gas reaction to give the material a high surface area, and then withdrawing the coke and impregnating it with tungsten or molybdenum sulfide.

In addition to impregnation, other methods of catalyst addition to the char may be used, for example, volatilization of the catalyst and condensation on the char, or spraying a solution of the catalyst onto the hot char, within the reactor.

While the foregoing description and exemplary operations have served to illustrate specific applications of the invention, other modifications obvious to those skilled in the art are within its scope.

What is claimed is:

1. The process of producing gas mixtures containing carbon monoxide and hydrogen which comprises passing a stream of finely-divided carbonaceous solid material into an initial water gas reaction zone, forming a fluidized mass of solids therein, subjecting said mass to a gasification reaction with steam at temperatures of from about 1500° to 2000° F. to produce a gas rich in H₂ and CO, withdrawing said gas from said water gas reaction zone, withdrawing from said water gas reaction zone, finely divided char of high surface area, passing at least a portion of said char into a catalyst impregnation zone, impregnating in said zone said char with a catalyst promoting gasification of carbon, recycling said impregnated char of high surface area to said water gas reaction zone and recovering a gas rich in H₂ and CO from said last-named zone.

2. The process of claim 1 wherein said catalyst is sodium carbonate.

3. The process of claim 1 wherein at least a portion of the heat requirements is supplied to said water gas reaction zone by withdrawing char from said water gas reaction zone, passing said withdrawn last-named char to a combustion zone, subjecting said last-named char to an exothermic combustion reaction to produce an ash having a high catalyst content and recycling at least a portion of said ash to said water gas reaction zone to supply both catalyst and heat for the endothermic gasification reaction.

4. The process of producing gas mixtures containing carbon monoxide and hydrogen from solid carbonaceous materials and steam, which comprises contacting steam at gasification temperatures with a dense fluidized mass of finely divided carbonaceous solids of initially relatively low surface area in a water gas reaction zone, forming a char of high surface area within said zone, and incorporating into said highly active char a catalyst promoting the gasification of carbonaceous materials by withdrawing a portion of said char from said reaction zone, impregnating at least a portion of said withdrawn char with said catalyst and recycling said impregnated portion to said reaction zone.

5. The process of claim 4 in which said catalyst is Na₂CO₃.

6. The process of claim 4 wherein said carbonaceous material of relatively low surface area is fresh coal.

7. The process of claim 4 wherein said carbonaceous material of relatively low surface area is a coke produced by the carbonization of coal at temperatures of about 800° to 1000° F.

8. The process of claim 4 wherein 0.1 to 3%

2,652,319

9

by weight of catalyst is incorporated into said char.

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10

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